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**EXPERIMENTAL ATTEMPT TO METALLIZE HYDROGEN
AT VERY HIGH PRESSURES**

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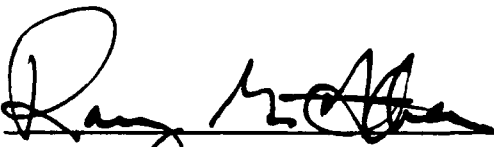
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13. ABSTRACT (Maximum 200 words) Metallic hydrogen is a potential candidate as a high energy density material. The possibility of metallizing hydrogen by submitting it to very high pressures has been experimentally investigated. Great advances have been made in this study. Pressures as high as 2.3 megabar on hydrogen have been obtained in diamond anvil cells (DACs). Several new phase transitions have been observed in the megabar pressure region. One of these, called the hydrogen-A (H-A) phase is believed to be the metallic molecular phase of hydrogen. However, current limitations on the optical techniques available to diamond anvil cell research have prevented direct determination of the conductive state and techniques for the direct measurement of the dc electrical conductivity are still under development. Band structure calculations have shown that metallization may be profoundly affected by molecular orientational order. Other observed phase transitions are believed to be associated with orientational order and fundamental changes in the molecular symmetry at high densities. A pulsed NMR system for studying very small samples of hydrogen has been constructed and will be useful in analyzing the nature of high density hydrogen.				
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EXPERIMENTAL ATTEMPT TO METALLIZE HYDROGEN AT VERY HIGH PRESSURES

SUMMARY

To study the metallic state of hydrogen, it is necessary to achieve pressures greater than one megabar. Achieving these pressures under careful laboratory conditions using hydrogen is now fairly routine. Since the inception of this contract, the maximum measured pressure attained for hydrogen and deuterium studies was 230 GPa.¹ Early in the program a new phase line was found to exist in hydrogen with a transition pressure of about 150 GPa in the zero temperature limit. The nature of this new phase has not yet been determined, but there is some evidence that it may be the metallic molecular phase (Fig. 1). We have named this the hydrogen-A (H-A) phase.

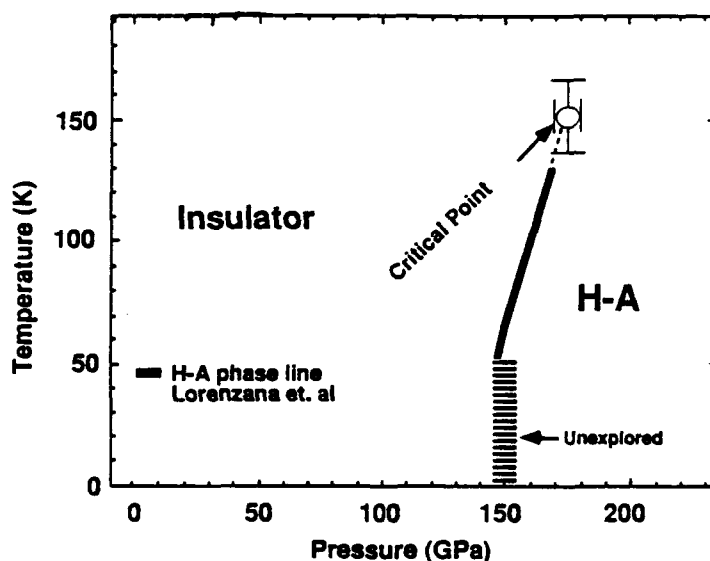


Figure 1

An Incomplete Phase Diagram of Hydrogen, Showing the Pressure Region of the New Hydrogen-A Phase.

At low pressure and temperature para hydrogen molecules are in spherically symmetric states. In spite of the fact that the underlying structure of the molecule looks like a dumbbell, the molecules are in ball shaped quantum mechanical states and cannot be orientationally ordered. At very high densities when neighboring molecules have a large degree of electronic overlap the molecular wave functions can abruptly change to a non-spherically symmetric state and the molecules can orientationally order. The resulting phase transition is called the rotational broken

symmetry phase (BSP). We have observed the BSP transition of para-hydrogen at 110 GPa. We also found a new phase of para hydrogen within the H-A phase. This phase is not yet identified, but we believe it is to be associated with orientational order. Studies using Raman scattering have also shown that when crossing into the H-A phase the molecules go from a state of orientational disorder to order.

In order to determine the nature of the H-A phase we made dielectric measurements on hydrogen to 73 GPa; these suggested, by extrapolation that the H-A phase might be the metallic molecular phase. Later experiments of ours to 220 GPa show that this interpretation is unclear. A more difficult measurement, which can in principle be used to determine the metallic nature of a sample, is to measure the reflection and absorption spectra as a function of pressure. Reflection measurements on hydrogen to 176 GPa were first published by Mao *et al.*² who claimed direct evidence for metallic hydrogen with an onset at 149 GPa, the pressure of the H-A transition. However, we studied hydrogen in reflection and absorption to 230 GPa and found no optical evidence of metallization. Mao *et al.* have now studied hydrogen in absorption and revise their earlier claim.³ However, they still make a weak claim of metallization. Our analysis of their results shows that their data does not warrant such a claim. At this point there is no experimental evidence that hydrogen has been metallized. However, there exists a great deal of tantalizing results which require extension to make a rigorous determination of the conductive state of the high pressure samples.

Crucial to any study of the high pressure hydrogens (hydrogen and its isotopes) is a determination of the pressure. At the outset of this study there was a great deal of difficulty and uncertainty in the use of the ruby spectrum as a pressure gauge in the megabar range. We have performed a number of studies to understand the spectrum, to separate the ruby spectrum from interfering background fluorescence from diamonds, and to improve the efficiency of excitation.

In the early stages of the program, time was devoted to the development of the diamond indenter technique (DIC). This technique may enable achievement of pressures greater than those achieved with DACs. Although some progress was made in this development, this work was deferred to the future as our current techniques were enabling us to achieve extremely high pressures and we wanted to devote our time to measurements using these techniques.

Early in the program a startling announcement of cold fusion of deuterium in palladium was made by Pons and Fleischman.⁴ We rapidly developed some new ideas for techniques to prepare enhanced samples of Pd loaded with D₂, using high pressure techniques. We discussed the possibility of devoting some time to this important energy area with the Air Force and reprioritized our work and program. Unfortunately we, along with the rest of the scientific community, achieved negative results when testing for cold fusion. We also discussed with the Air Force the indefinite deferral of research on H₂:H alloys. This was originally conceived as a means of achieving metallic hydrogen at a lower pressure than could be achieved in pure hydrogen. Due to our rapid progress with the pure material it was more important to concentrate our efforts on hydrogen and its isotopes. Construction of a new diamond anvil cell has been deferred to the end of the program. Also the development of NMR was deferred. The current status is that a cryogenic system

with an NMR magnet has been built along with a DAC support system for the cryostat. The NMR electronics for pulsed Fourier spectroscopy has been built along with a fast digitization system and tested with a computer interface. The apparatus is currently being tested by doing NMR on well known samples (hydrogen at zero-pressure).

INTRODUCTION

This project was initiated with the primary goal of producing metallic hydrogen in the laboratory. This can be achieved by submitting solid molecular hydrogen to pressures in the megabar range using diamond anvil cell (DAC) techniques. Theoretically, hydrogen remains the most important chemical fuel for rocket propulsion due to its large specific impulse. Currently, it is used as a fuel, burned in combination with other chemicals such as oxygen. If hydrogen could be produced in a stable form as metallic hydrogen it would be a major breakthrough for future propulsion fuels. In the metallic form hydrogen stores substantially more potential energy than in the liquid molecular form, essentially the energy of formation. Secondly, the molar density is 11 to 12 times greater than that of the liquid so that the demands of fuel storage are greatly relaxed, improving vehicle performance. Although it is suspected that metallic hydrogen may have been produced in the laboratory in recent experiments, there exists no rigorous proof at this time.

In 1935 it was predicted by Wigner and Huntington⁵ that at a sufficiently high density solid molecular hydrogen would undergo a (dissociative) phase transition to an atomic metallic state. The transition pressure was believed to be about 25 GPa (100 GPa=1 megabar); modern calculations such as the Green's function Monte Carlo work of Ceperley and Alder⁶ predict this transition to take place at 300 to 400 GPa. A great stimulus to produce this substance in the laboratory was given to scientists by Ashcroft's⁷ 1968 prediction that atomic metallic hydrogen would be a high temperature, possibly room temperature, superconductor. This has been supported by more modern electron-phonon interaction calculations,⁸ using the BCS theory.

In the 1970's a number of new ideas emerged. It was believed, based on calculation⁹ that metallic hydrogen would be a metastable material, much like diamond, so that once formed under great pressure, it would remain in the metallic state when the pressure was released. A later calculation by Salpeter¹⁰ predicted that this metastable substance would rapidly transform back to the molecular phase at zero pressure. Of course, the ultimate test of the metastability of metallic hydrogen will be in the laboratory. Another prediction was that metallic hydrogen might be a liquid at $T=0$ K due to the large zero-point energy of the atoms.¹¹ The most relevant predictions for the current research has been a deeper understanding of the path to metallization. It was realized by Ramaker *et al.*¹² that preceding the dissociative transition, hydrogen might first metallize in the high density molecular phase due to band overlap. Recent calculations¹³⁻¹⁵ predict this transition to fall in the 150 to 300 GPa range.

Thus, theoretically as hydrogen is pressurized one expects it to first become metallic in the molecular phase, and then at a higher pressure to have a second transition to the atomic metallic phase. Hydrogen has isotopes of deuterium and tritium and mixed molecules such as HD can be produced. Although at low pressure the isotopes have important differences, this is due mainly to the zero-point energy which is comparable to the potential energy of the intermolecular interactions. At high pressure the latter dominates the zero-point energy and since the isotopes are isoelectronic we do not expect important differences in the metallization pressure of the isotopes. It may well turn out that for technical reasons it will be easier to study deuterium than hydrogen.

We also mention that due to the identical nature of the constituent nuclei, hydrogen and its isotopes have two species, ortho and para, depending on the coupling of the nuclear spins. Due to spin statistics for identical particles the hydrogen molecular wave function must be antisymmetric under nucleon permutation and deuterium must be symmetric. The consequence of this is that the ortho-H₂ species have odd rotational states and para H₂ have even rotational states.¹⁶ It has recently been realized that the orientational order of hydrogen or deuterium (which depends on the rotational states) may have a profound effect on the insulator-metal (IM) transition. Thus, it is extremely important to characterize the ortho-para content of a crystal and the conversion rates between species. This can most easily be accomplished by NMR studies. Finally, we note that a crystal of HD should also be metallizable. However, HD differs in a few ways. First since the constituent nuclei are not identical it does not have ortho and para species. Second, at very high densities we might expect some rearrangement by exchange of nucleons so that the HD transforms to H₂ + D₂ + HD.

EXPERIMENTAL METHODS FOR GENERATING MEGABAR PRESSURES

In this section we briefly review the techniques that we have used and developed for producing megabar pressures on solid hydrogen and making spectroscopic measurements on the samples to determine their properties. One of the important hallmarks of our development of the diamond anvil cell technique is the marriage of high pressure with low temperature. The latter is used both in the loading of samples (cryogenic loading) and the study of their properties.

The basic configuration of a DAC in a cryostat which we use¹⁷ is shown schematically (Fig. 2). The DAC sits in a chimney like tube in the cryostat and the high pressure region can be optically accessed via windows in the cryostat tail. Reservoirs can be filled with either liquid nitrogen or helium. A small amount of helium gas can be introduced into the chimney to thermally couple the DAC to the cryogens for cooling, or when evacuated the DAC can be heated to a desired temperature. While the DAC is at temperatures near absolute zero Kelvin the pressure can be changed by finger turning a screw via a shaft which protrudes out the top of the cryostat. The DAC is shown in more detail (Fig. 3). The screw is connected to a follower nut on a wedge; as the wedge advances a diamond on a cylinder is advanced towards a rigidly mounted diamond for the pressure generation stroke (Fig. 3, right hand side). Samples of hydrogen are cryogenically

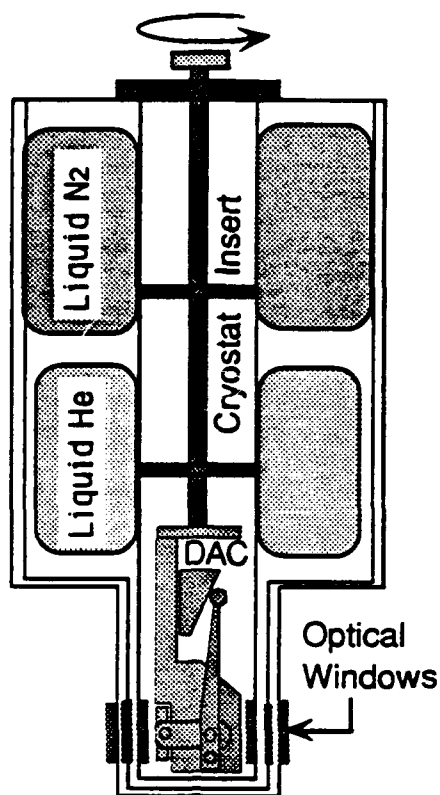


Figure 2

A Schematic Diagram of a DAC in a Cryostat with Optical Access.

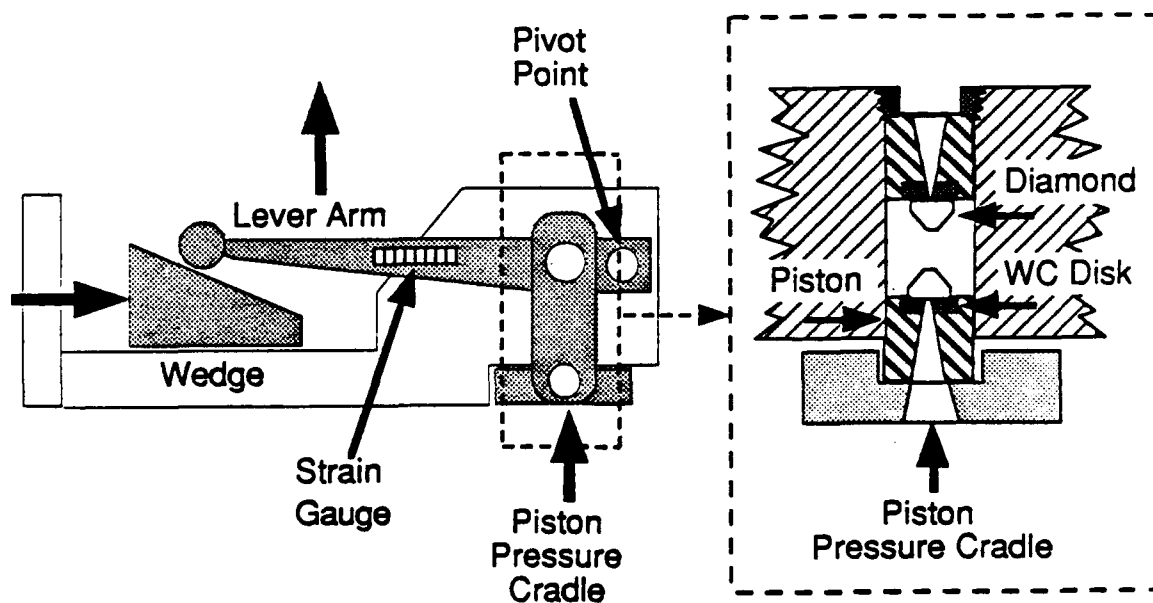


Figure 3

The General Design of the DACs Which can be Remotely Pressure Tuned. On the Right, the Heart of the DAC is Shown in Cross Section.

loaded into a mini-chamber built around the diamonds (Fig. 4). The diamonds are sealed in two brass hats which are closed off by a sliding teflon seal. The DAC is cooled to the liquid region of the hydrogen phase diagram and the minichamber is filled with liquid hydrogen. The gasket hole is filled with hydrogen and the diamond is then advanced to seal on the deformable gasket and compress the sample. In advance of loading, ruby grains are placed on the diamond culet (Fig. 5); these are compressed along with the sample and used for pressure determination.

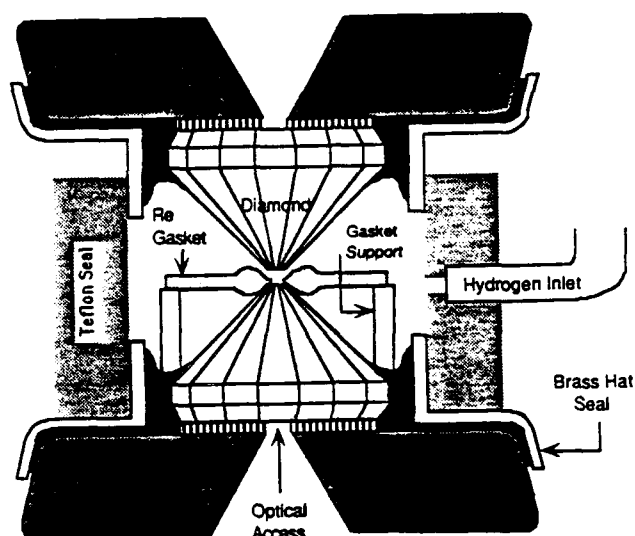


Figure 4

The Diamond Anvils Situated in a Minichamber used for Cryogenic Loading of Samples of Hydrogen.

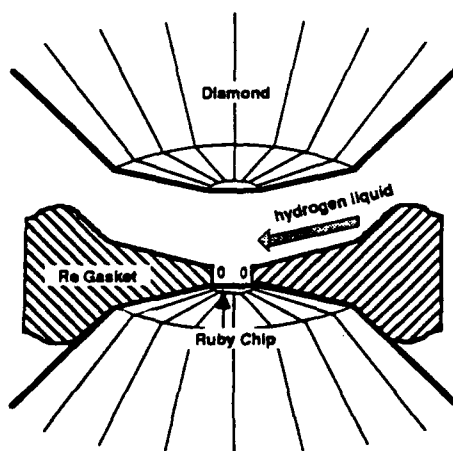


Figure 5

Detail Shows Location of Ruby Chips, Diamonds and Liquid Hydrogen.

In order to achieve megabar pressures, substantial care is required. We use diamonds rich in nitrogen platelet impurity. The diamond culets are 50 to 75 microns in diameter and double beveled. Fig. 5 shows a single bevelled set of diamond anvils. It is very important that they oppose each other and culets are parallel. These adjustments are made optically, using interference techniques before loading. Holes in the rhenium gaskets are made by electric discharge machining techniques and are of order 25 to 50 microns in diameter and located to a precision of about 2 microns. To reach high pressures, the DAC must be well constructed so that during the pressure stroke the diamonds maintain their alignment.

An optical set-up used for Raman scattering was developed (Fig. 6).

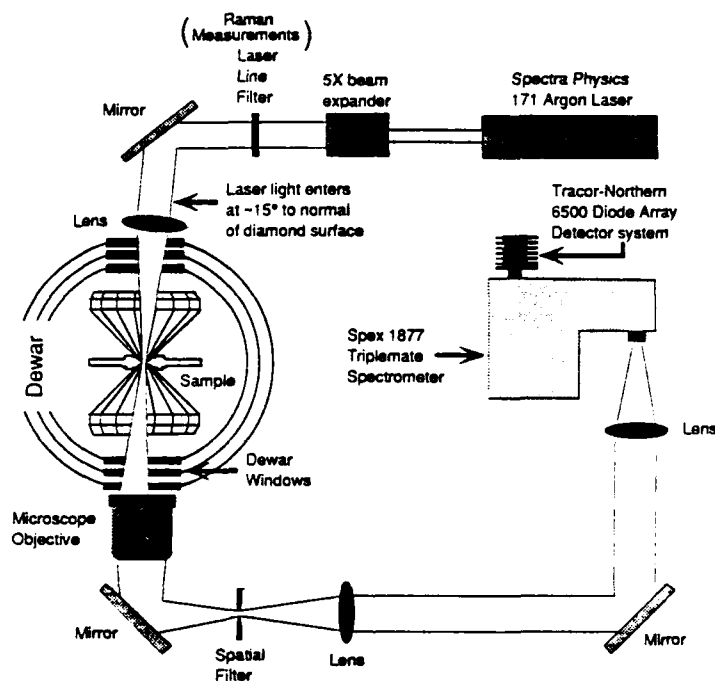


Figure 6

Optical System Diagram to Collect Signal from Sample.

The beam expander allows the laser beam to be precision focused. The spatial filter on the collection side is for suppression of fluorescence signal from the diamond. The latter gives a large background creating serious signal-to-noise problems at high pressure. In general, intensified diode arrays are used for the optical measurements. These have enabled us to produce a large number of results in the past few years, and for many measurements arrays relegate the single photomultiplier to a spectroscopic technique of the past. A different optical set-up is used for measuring optical reflection and absorption in hydrogen. The laser is replaced with a white light source and the spatial filter is used to select the region of interest in the sample. Using spatial filters and precision microscopy we can measure the optical properties of a 5 micron diameter region of a sample.

THE HYDROGEN-A PHASE

In 1988 Hemley and Mao¹⁸ observed a phase transition in hydrogen at about 155 GPa. This was noted from a discontinuity of the frequency of the Raman active vibron upon changing phase. At zero-pressure ortho-hydrogen has a transition from orientational disorder to order at $T=2.8\text{K}$; para-hydrogen has no orientational order transition.¹⁶ The transition takes place due to the electric quadrupole-quadrupole (EQQ) interaction which has a lower crystal energy in the ordered state. With increasing pressure the critical temperature increases. Hemley and Mao interpreted the high pressure transition as an extension of the low pressure EQQ ordered phase. However, they measured over a broad temperature range (77-130 K) and up to pressures of 200 GPa, but only reported a single point on the phase line at 155 GPa and 77 K, whereas over this broad range of temperature and pressure a phase line should have been traced out. Moreover, the interpretation of the data did not account for the fact that the sample was nominally 50-50 ortho-para.

We studied a hydrogen sample in the temperature range 5-140 K and up to a few hundred GPa pressure, concentrating on the vibron spectra (Fig. 7). We observed the vibron discontinuity, the Raman intensity, as a function of frequency

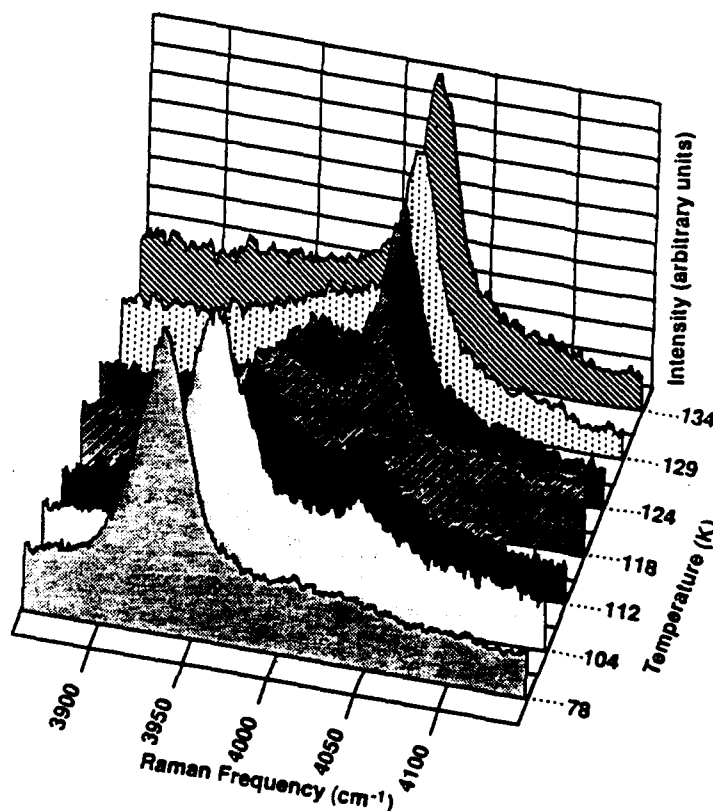


Figure 7

Raman Spectra Showing the Thermal Behavior of the Vibron near the H-A Transition in Solid H_2 at a Pressure of 164 GPa. The Low Temperature Peak is the H-A Vibron.

for several temperatures at a fixed pressure. To interpret this data we determined that the sample had a pressure distribution of about 5 GPa. As a consequence, when in the vicinity of the phase line, part of the sample would be in the high pressure phase and part in the low, giving rise to two vibron lines. Well above or below the phase line there is but one vibron line. From a simple model including the pressure distribution, it was easy to show that the critical temperature is the temperature at which both vibrons have equal intensity. This determines a P,T point. Similar studies for different pressures enabled us to determine the phase line (Fig. 8). In this figure the solid triangles represent the measured phase boundary. The open squares indicate $P-T$ points in which the sample was established to be completely in the low-pressure phase, whereas it was completely in the high pressure phase for the filled squares. The open triangles denote the $P-T$ points for which there was no spectral evidence of the new phase in cooling down from 77 to 4.2 K. These results demonstrate that the new phase exists only for pressures above about 150 GPa. Moreover, to within experimental error the phase line was found to

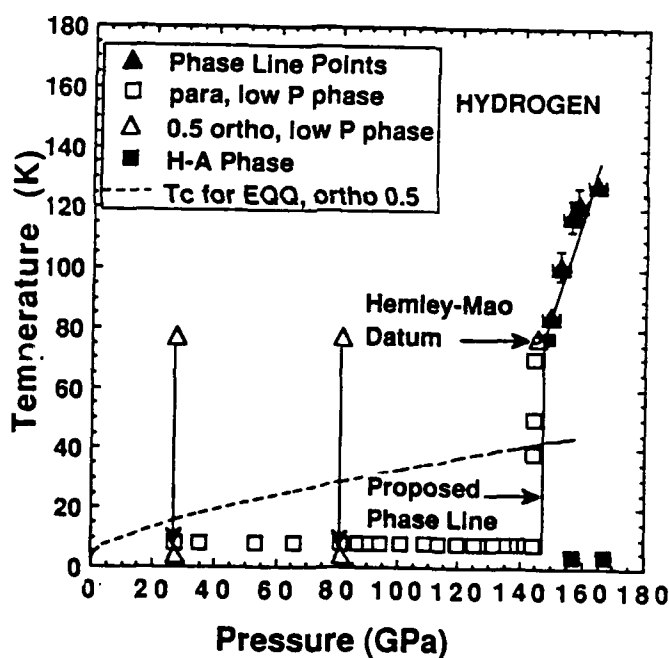


Figure 8

The Proposed $P-T$ Phase Diagram for Hydrogen.

be independent of ortho-para concentration. Both of these results are inconsistent with the new phase being an extension of the low pressure phase of orientational order, although the new phase might also be characterized by orientational order. Thus, this must be a different phase which we named the hydrogen-A (H-A) phase.

The intriguing possibility existed that the H-A phase was the molecular metallic phase (molecular because vibron modes characteristic of molecules still

exist in the high pressure phase). It occurred at pressures expected from theory, with the phase line rising steeply with pressure. Moreover, in the H-A phase the vibron shifts down in frequency by about 100 cm^{-1} , which is a very large shift for a pure orientational order transition. Such a shift would be consistent with metallization. In this case electronic charge is transferred from a proton-proton bond into a conduction band. This weakens the bond, and thus the vibron or bond frequency shifts down.

One more interesting observation has been a critical point termination of the H-A phase line, observed in two different laboratories.¹⁹ The H-A phase transition is characterized by a large frequency discontinuity, 100 cm^{-1} at the pressure onset of the transition. However, at higher pressures and temperatures the discontinuity decreases in size. At about 170 GPa and 155 K it goes to zero. Beyond these values one can go continuously from one phase to the other, as in the critical point of water. Thus, the phase line terminates in a critical point (Fig. 9). Silvera²⁰ has proposed a model which could explain this critical point in terms of a combined order-disorder IM transition.

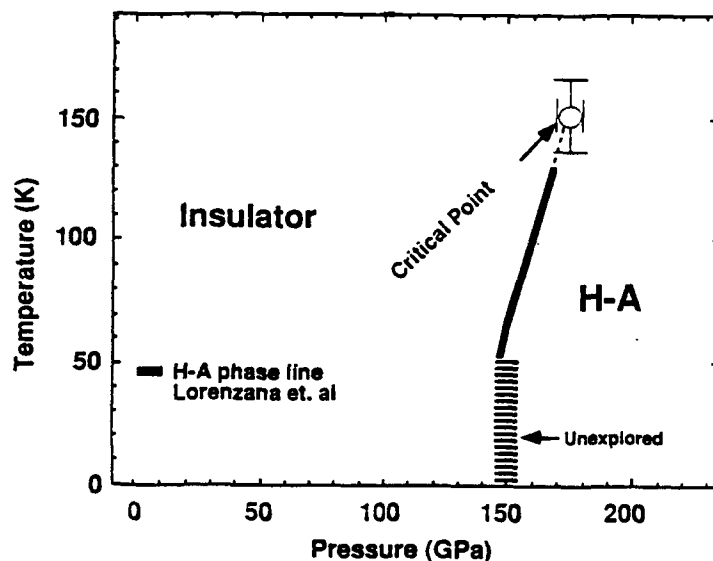


Figure 9

The H-A Phase Line Showing the Critical Point.

ORIENTATIONAL ORDER TRANSITIONS

To identify the H-A phase it is important to eliminate other expected phase transitions. From earlier studies²¹ the BSP phase transition was expected to occur in the megabar pressure range. To search for the BSP transition²² we prepared a parahydrogen sample by holding a high pressure sample of hydrogen at 5K for 24 hours. This enabled the sample to convert to the equilibrium para species, almost 100%. We studied the Raman and vibron spectra as a function of pressure at 5 K. An

abrupt change in the spectrum at 110 GPa has been interpreted as the BSP transition and a point on the phase line has been determined (Fig. 10). This figure includes data for *p*-H₂ and ~50% ortho mixtures. The dashed line from the SP (Symmetric-Phase) BSP phase-line point is an indication of the expected the phase line. The dashed line from the ordered *p*-A phase line is a linear extrapolation. Unfortunately the pressure was raised stepwise while at T=5 K so that the phase line for the BSP phase was not determined. Later, it was not possible to reduce the pressure, as this results in failure of the diamond anvils. It will be necessary to return to this pressure-temperature region in the future to determine the details of the phase line.

The same sample was pressurized into the H-A phase and then the temperature was rapidly raised, in times much faster than the ortho-para conversion time. The Raman spectrum was found to change abruptly above a certain pressure. The locus of such P,T points determine a phase boundary (Fig. 10). The nature of this transition is not known.

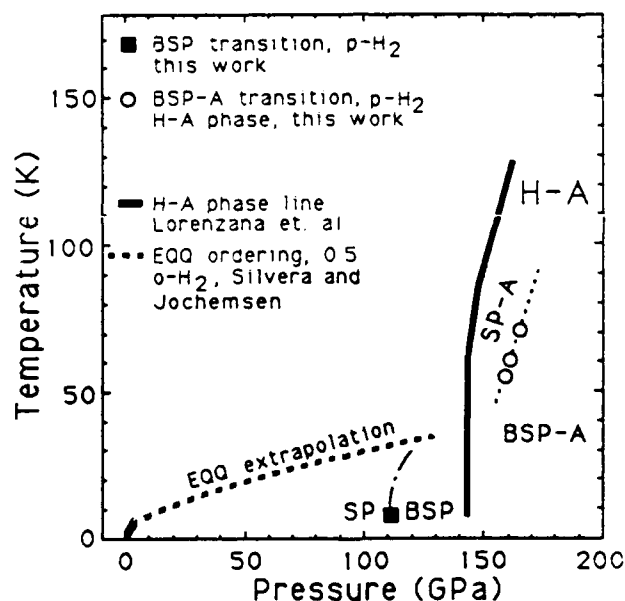


Figure 10

Proposed High-Pressure Phase Diagram for Hydrogen.

While in the H-A phase the sample was held at 77 K to convert to equilibrium, 50-50 ortho-para. When the temperature was raised so that the sample went into the low pressure phase the Raman rotational lines broadened severely. This broadening was interpreted as due to orientational disorder. Thus, under our interpretation, upon entering the H-A phase molecules orientationally order. We still have not determined what happens to the electrons, i.e. do they form conduction bands? In our measurements, the sample was held at a fixed pressure

and the temperature was varied to determine this latter effect of order-disorder. Hemley *et al.*²³ also studied hydrogen in this range. They kept the temperature fixed at 77 K and varied the pressure and did not report evidence of orientational order. Thus, there is evidently some complicated behavior in the properties which will require very careful study in the future.

DIELECTRIC STUDIES OF HYDROGEN

In the insulating phase of a material being studied for an IM transition, one can determine the critical pressure by measuring the optical absorption. For a direct band gap insulator the absorption coefficient for electronic transitions is zero until the photon energy equals the band gap energy, and then it rises steeply. For an indirect band gap transition, in order to conserve crystal momentum the photon creates a phonon excitation along with an electronic valence to conduction band transition. This second order process is much weaker than a direct band transition; nevertheless, since the phonon energies are quite small, the absorption energy can still be used to determine the band gap. One can then measure the band gap as a function of pressure and determine the pressure at which the gap closes, i.e. the metallization pressure. The latter usually must be determined by extrapolation. The difficulty with this procedure in hydrogen is that at zero pressure the band gap transition is about 16 eV (in the UV) at an energy for which the diamond windows are strongly absorbing, preventing such measurements.

The problem of absorbing diamonds can be circumvented by measuring the dispersion of the index of refraction in the visible. The dispersion is related to the high frequency absorption and can be analyzed using a "single oscillator" model.²⁴ In order to perform the measurement of the index one can take advantage of the fact that the diamonds are aligned with their flat culets parallel to each other so that the diamonds form a Fabry-Perot resonator filled with hydrogen. The resulting fringe pattern has a spacing $1/2nd$, where n is the index and d the thickness of the sample. After observing the H-A phase, such measurements were carried out on hydrogen to 73 GPa.²⁴ An extrapolation to determine the critical pressure gave a result in the region of 150 to 200 GPa, lending indirect support for the idea that the H-A was the metallic phase of hydrogen. Later these measurements were extended to 220 GPa,²⁵ beyond the region of validity of the single oscillator model. Since the results are outside of the region of validity of the single oscillator model and difficult to interpret, we have collaborated with the Cohen group at Berkeley to do a sophisticated calculation of the dielectric function of hydrogen. Results still do not allow a firm conclusion to be drawn concerning the conductive state of the sample (Fig. 11). This is a consequence of our lack of knowledge of the high pressure crystal structure of hydrogen and also of the crystal orientation of the sample. A model calculation shows that measurements should be very sensitive to both the photon polarization and the state of orientational order of the molecules. We see very good agreement with experiment for one polarization, but poor agreement for the other (Fig. 11). In this figure (solid lines marked (O)x and (O)z are for hcp-c oriented crystals; broken lines marked (S)x and (S)z are for hcp-spherical molecule crystals (S)), these

theoretical results are compared with experimental data. We believe that some of these ideas may be further tested by measuring the dispersion for different ortho-para mixtures, which should have different degrees of orientational order.

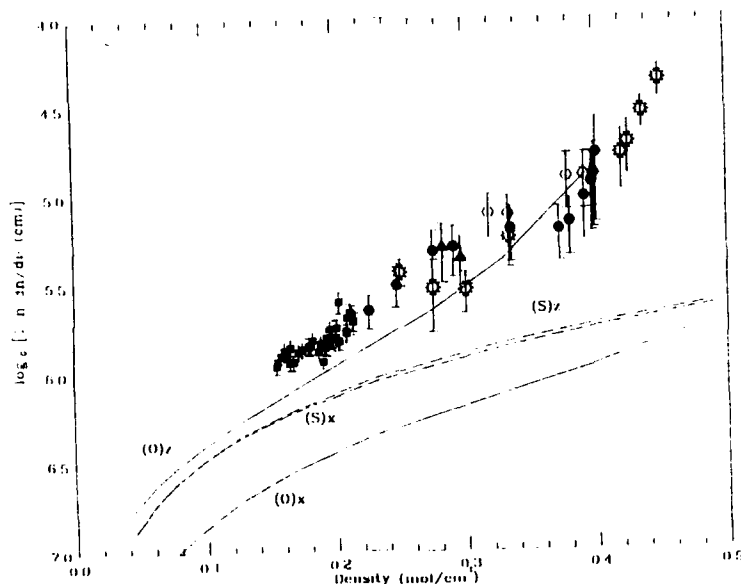


Figure 11

Calculated $(1/n)dn/dv$ as a Function of Density.

THEORETICAL CONSIDERATIONS OF THE ELECTRONIC STRUCTURE OF HYDROGEN

The rapid experimental development of properties of hydrogen at high pressure opened a number of important theoretical questions. Early calculations of the electronic band structure of hydrogen²⁶ used the Pa3 structure without any basis for this choice. Furthermore, the local density approximation (LDA) was used which is very good for calculating total crystal energies, but is notoriously bad for calculating band gaps, giving gaps about a factor of two too small. These early calculations predicted metallization at a few hundred GPa, perhaps fortuitously. Later Barbee *et al.*²⁷ found the hcp lattice to have a lower energy than Pa3. Theoretical metallization pressures were well under 100 GPa, using the LDA. These calculations did not take into account the rotational state of the molecules, but rather used a ball and stick model of molecules; Ashcroft²⁸ had shown on general grounds that the orientational order might have a substantial effect on the electronic structure.

We performed a calculation in collaboration with the Cohen group at Berkeley.¹³ First the LDA was extended with the Slater x-alpha method to give a semiempirical calculation by fitting the x-alpha parameter to give the correct experimental zero pressure gap. Using an hcp lattice with molecules oriented along the c-axis (hcp-c), a transition pressure of 180(20) GPa was predicted, very close to the H-A pressure (Fig. 12). A calculation was also done by replacing the oriented molecules with sphericalized molecules to represent the orientational disorder. This raised the critical pressure to 400 GPa demonstrating the sensitivity to orientational order.

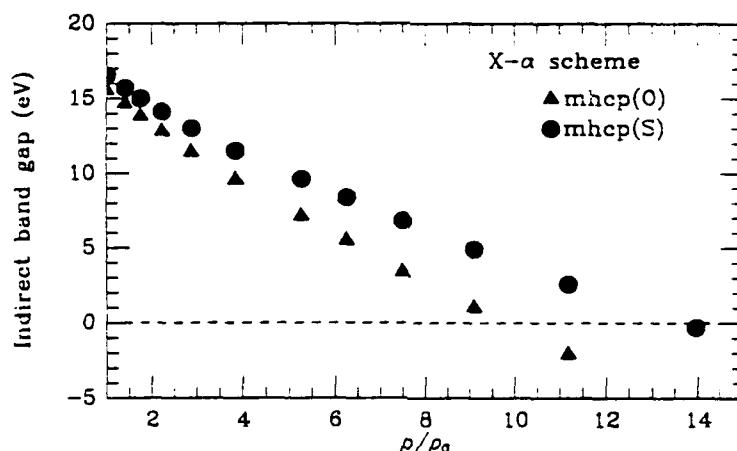


Figure 12

The Indirect Band Gap in Hydrogen for an hcp-c Oriented Crystal (Triangles) and hcp with Spherical Molecules (Circles).

More recently Kaxiras *et al.*¹⁵ have reconsidered this problem. They find a structure of lower symmetry, with molecules on the hcp lattice oriented away from the c-axis, having a lower energy than hcp c-oriented, and thus should be the favored structure. However, the predicted pressure for band gap closure is substantially higher than the pressure of the H-A transition. This result has thrown the theoretical picture into disarray. A particularly restrictive problem is the experimentally unknown crystal structure. In normal solids molecules do not rotate and the zero-point motion is small. In hydrogen, for the first time electronic structure calculations have run into the serious problem of the rotational states for wavefunctions and the formalism does not exist for handling these motions. Furthermore, there does not exist a method to accurately calculate the effects of the large zero-point motion. These represent challenging problems for the theoretical community.

OPTICAL ABSORPTION AND REFLECTION IN HYDROGEN

One of the most important experimental optical techniques for demonstrating that a sample is in the metallic state is to measure the optical reflection and absorption. The simple Drude free carrier model of metals gives a surprisingly accurate description of experiment. In this model there are three parameters: the plasma frequency, ω_p , the scattering time τ , and the real part of the dielectric constant ϵ_0 . The plasma frequency is proportional to the square root of the free carrier density, thus at the critical pressure this quantity goes to zero. The Drude model has a very easily recognized behavior for metals: above the plasma frequency, the reflection goes to zero (or the value due to ϵ_0) as does the absorption. For energies below the plasma frequency the absorption rises steeply and the reflection approaches 1. For a metal, one would then expect a rising edge in reflection and absorption, which shifts to higher frequency with increasing pressure (which should increase the carrier density).

Mao, Hemley and Hanfland² (MHH) published an article claiming to have definitive proof of metallization of hydrogen at 149 GPa. This was based on the Drude behavior observed in their reflectivity measurements, with pressures up to 176 GPa. Simultaneous with this publication, at Harvard we had a sample at higher pressures, going to 230 GPa, which did not show Drude behavior in either absorption or reflection. It was unclear if we had a sample of hydrogen in a different, possibly metastable state, or some more subtle problem was giving rise to these differences in the two laboratories. However, our reanalyses of MHH's results showed their data to be inconsistent with their interpretation and Drude parameters² (Fig. 13). In this figure the dotted line is the absorption according to MHH's Drude parameters. This absorption should result in attenuation of the fringes, as shown by the solid line, using Fabry-Perot theory with the sample in the cavity having the Drude absorption. This leads to the conclusion that the MHH Drude constants must be incorrect. Our results, in which the optical absorption was measured as a function of photon energy in hydrogen at 77 K and for various pressures established that to 230 GPa there was still no evidence that hydrogen had been metallized (Fig. 14). The Drude model predicts a rapidly rising absorption at low energy. Our measurements show no absorption and are compared to the Drude model using the Drude parameters of Mao *et al.* In the curves shown in this figure the rise at higher energy is due to absorption in the diamond anvils. The dashed curves are the expected absorption calculated from the Drude model of Mao *et al.* (Fig. 15a). The absorption for several temperatures is also shown (Fig. 15b).

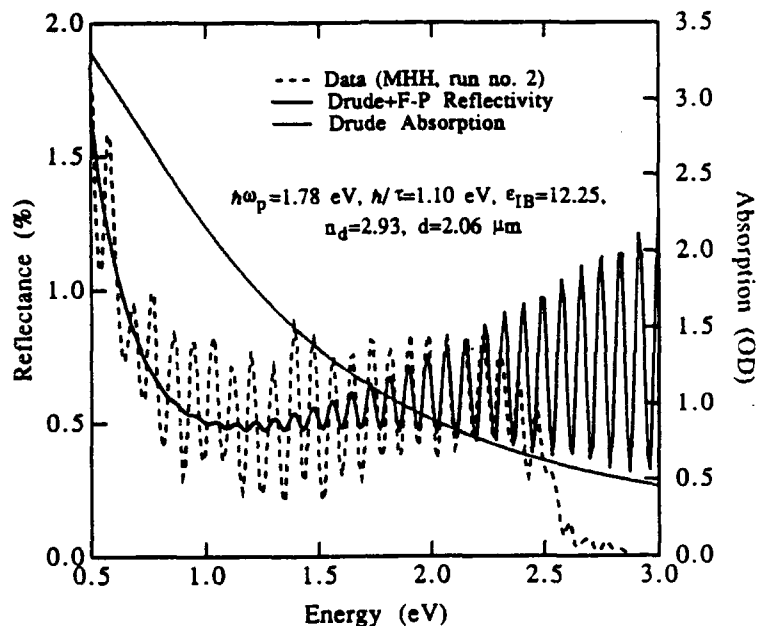


Figure 13

The MHH Reflectivity Data (Broken Line) and Curves Representing Theoretical Models.

The critical problem in MHH's result was that their Drude parameters predicted a much larger absorption than was observed by us. They then published an article on their absorption results³ confirming that the values were substantially too small to support their original claim of metallization. In order to explain both the absorption and reflection data, they greatly revised their Drude parameters although these values are not presented in the publication. They again claim that their optical results are consistent with metallization of hydrogen. In order to fit their data for both reflection and absorption it was necessary to assume that at the pressures of metallization the index of refraction of diamond is greater than that of hydrogen (the index change at the hydrogen diamond interface is an important parameter in the theory) which, however, is highly unlikely.

We have refuted this new claim, based on known values of the dielectric constants.²⁹ Diamond has an index of about 2.4 at zero pressure; electronic band structure calculations show that with either increasing pressure or stress the index decreases and remains below 2.4 to greater than 200 GPa. Hydrogen has an index of

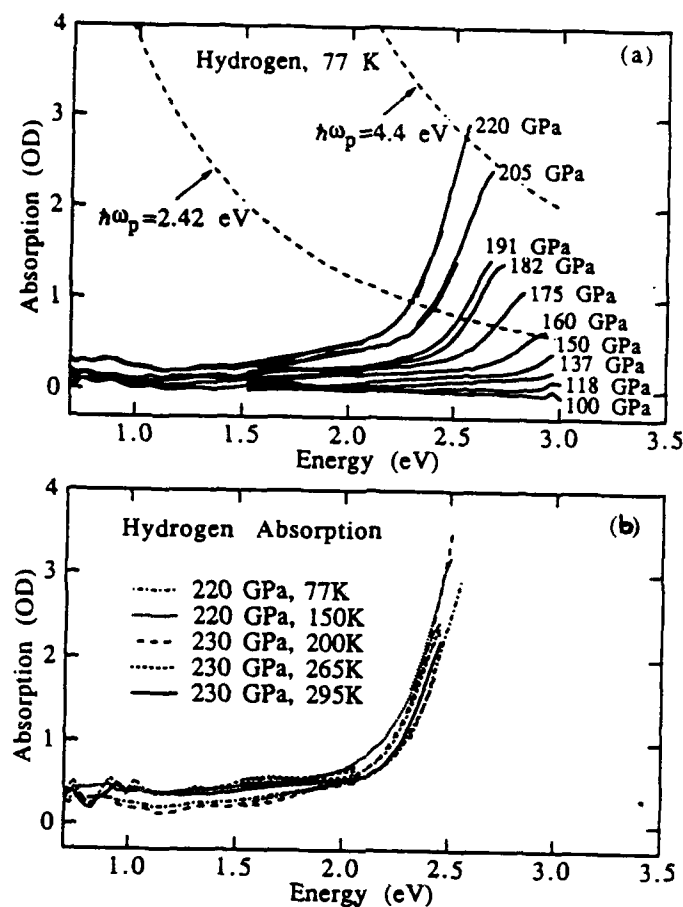


Figure 14

The Absorption in Terms of OD [$\log(I_0/I)$] Versus Photon Energy at Various Pressures in Hydrogen.

1.13 at zero pressure and increases rapidly with density (Fig. 15). We show a curve fit to measured values for hydrogen and extrapolated to higher pressures. The index of diamond, n_D , at high pressure has not been measured and the shaded area in the figure represents the uncertainty in theoretical values of n_D . One more point can be put on the curve by noting that optical interference measurements show that hydrogen and diamond index match at 130 GPa. This gives a very clear indication that the index of hydrogen is greater than that of diamond in the higher pressure regions, contrary to the assumption of MHH.

Although the optical technique is an excellent one, in general, for determining IM transitions, the measurements must be made to frequencies substantially below the plasma frequency. The present measurements were limited to about two microns wavelength. Clearly it is important to extend the spectral region of study.

At this time the question of metallization of hydrogen at very high pressures is unclear, both theoretically and experimentally. It is still possible that the H-A phase is the metallic molecular phase of hydrogen. However there is no direct evidence to support this. What then is the H-A phase, if not metallic? Understanding the nature of this phase constitutes a serious intellectual challenge that must be met.

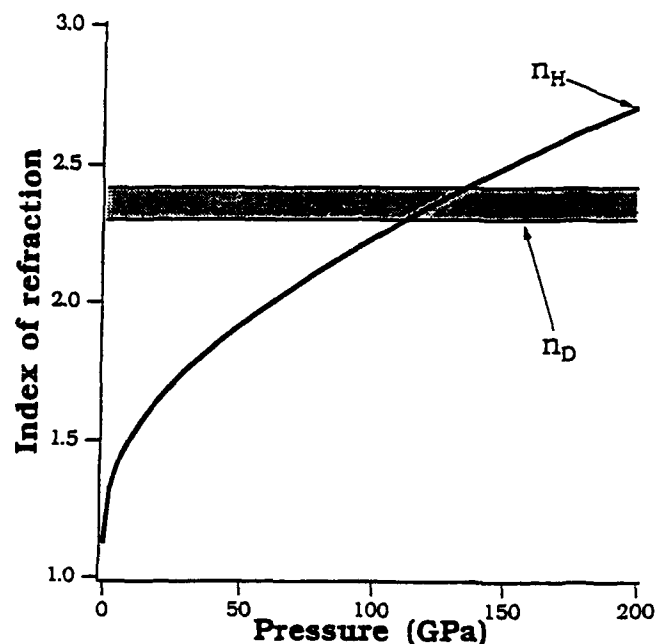


Figure 15

The Projected Index of Refraction of Hydrogen (n_H) and Diamond (n_D) for Very High Pressures.

OTHER TESTS OF METALLIZATION

The most rigorous test of metallization is to experimentally demonstrate that the dc electrical conductivity remains finite in the limit that T goes to zero. To make such measurements in a diamond anvil cell are challenging. The problem is to attach electrical contacts to a sample which at high pressure has dimensions of order 10-20 microns in diameter and 1-2 microns thick. Furthermore the leads must be insulated from the gasket through which they pass and must stand the large stresses. Although many of these problems have been solved in earlier measurements (our record is 70 GPa) hydrogen is more demanding as the leads are attached at low pressure and must withstand a change in volume of the sample of an order of magnitude.

In the past year we have been developing new types of leads in which the gasket is split into three parts: conductive layer, insulating layer and conductive layer, so that the two outer conductors are the contacts to the sample. The current is then forced to pass through the sample giving a measurement of its resistivity. Such leads require micromachining techniques and great care to assemble. At this time we have tried three different designs. All of these have failed, either by shorting out under load, or by the insulating layer extruding into the sample hole, preventing measurements. It is our intention to pursue improved designs, as such measurements would provide definitive evidence of metallic hydrogen.

PRESSURE MEASUREMENTS IN A DAC: THE RUBY SPECTRUM

One of the major reasons for the rapid advance of high pressure physics with the DAC has been the ruby pressure scale which provides a fast, easy, reliable means of determining pressure. At the beginning of this contract a great deal of doubt existed concerning the utility of the ruby scale at megabar pressures. It was found that the ruby fluorescence line broadened, severely weakened and suffered from a poor signal to noise ratio due to large interfering fluorescence from diamond. It had been found that above about 150 GPa the interference made it almost impossible to detect the ruby signal. Further there was some possibility of ruby line crossings, so that one could suffer from detecting the wrong ruby line.

We first were able to develop a time resolved technique which enabled us to suppress the diamond fluorescence by about 6 orders of magnitude so that the ruby could be followed to higher pressures.³⁰ This is best demonstrated graphically (Fig. 16). A weak ruby signal at a pressure of 138 GPa, superimposed upon a sloping diamond fluorescence background, is isolated when our chopping technique is employed. We then performed a study of the total ruby spectrum and developed an understanding of this in terms of ligand crystal field theory. We were able to fit and show how line crossings would occur in the ruby spectrum as a function of pressure.³¹ To facilitate

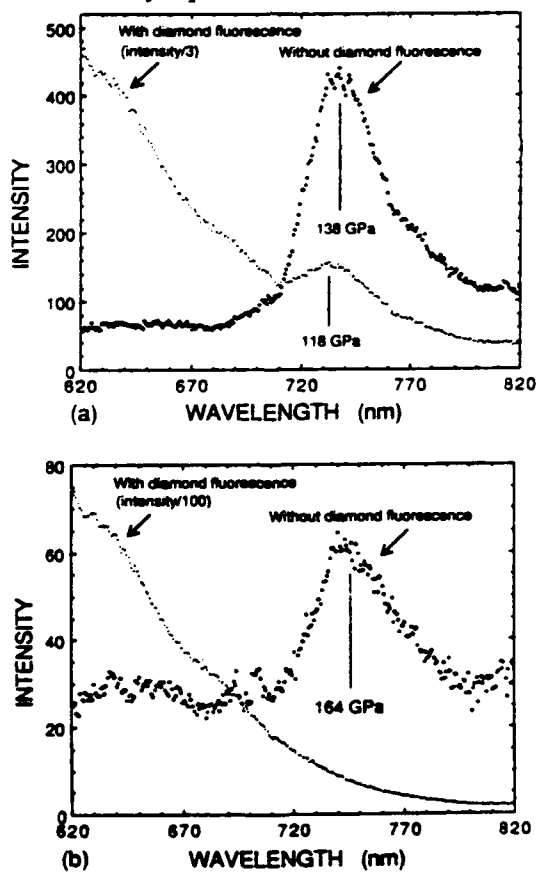


Figure 16

Demonstration of the Elimination of the Diamond Fluorescence.

comparison of spectra at different pressures, the frequency relative to the R_1 -line frequency at each pressure is plotted (Fig. 17). The R_1 line shifts with pressure. In the figure, the spectra are normalized to their maximum intensities and vertically offset for clarity. We then studied the ruby fluorescence lifetime as a function of pressure to about 200 GPa. We determined that the lifetime increased rapidly with pressure, which provided an explanation for the weakening of the ruby fluorescence

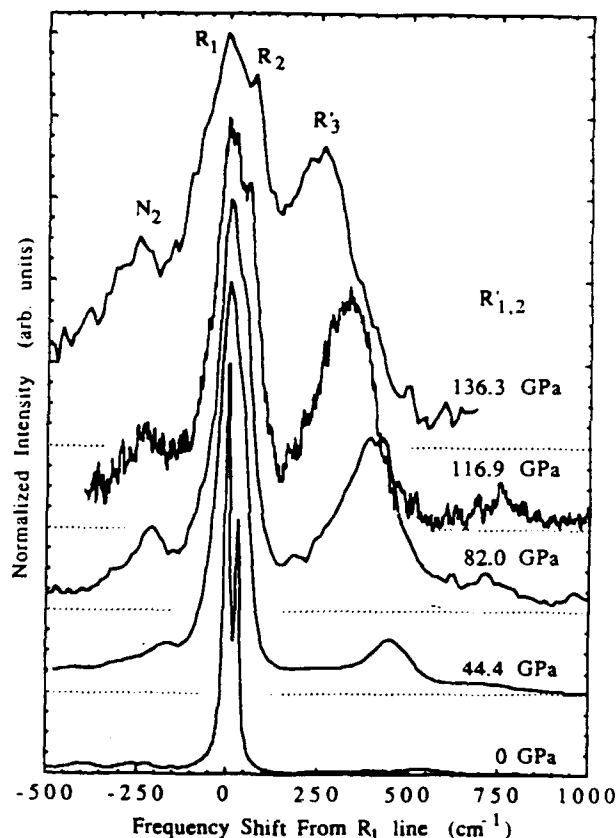


Figure 17

Ruby Fluorescence Spectra at Various Pressures in the Quasihydrostatic Pressure Medium.

with increasing pressure.³² Our most recent study has concentrated on the means of increasing the intensity of the ruby fluorescence signal.³³ In this case we studied the efficiency of excitation of the ruby fluorescence as a function of the frequency of the laser light. The principle result was that above 230 GPa ruby is much more intensely excited using the 4960 Å line of the argon ion laser. This enables determination of pressures based on ruby, which we believe will be useful to 300 GPa or higher.

PRESSURE DEPENDENCE OF THE VIBRON IN THE HYDROGENS

For more than a decade there has been intense interest in the pressure dependence of the vibron, not only for its utility in detecting phase transitions, but for its importance in elucidating the interactions and the possibility of nearing the region of metallization, since the mode frequency is dependent on the electronic charge between the protons. The Raman frequency rises steeply with pressure and then at about 30 GPa turns over and decreases (Fig. 18). This turnover has been thought to be a precursor of metallization, due to bond weakening correlated with

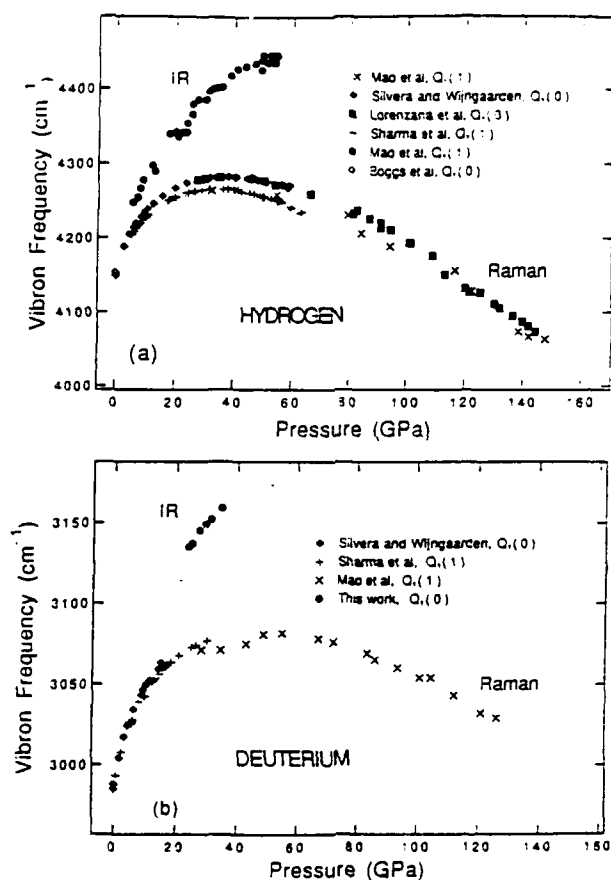


Figure 18

The Raman and IR Active Mode Frequencies as a Function of Pressure in Both Hydrogen and Deuterium.

charge transfer. This idea has been discussed in several places in the literature, however without theoretical justification. We noted that the IR active vibron of hydrogen continued to rise in frequency with increasing pressure. We also measured the IR vibron in deuterium and found the same result.³⁴ Thus, a detailed analysis of the modes was required. The lattice dynamics had been studied by van

Kranendonk³⁵ many years ago. His analysis showed that the IR mode frequency is mainly determined by the intramolecular potential and the turnover in the Raman mode is due to the intermolecular potential. Since the intramolecular potential is representative of the single molecule and the IR mode does not turnover, evidently there was no evidence of "charge transfer" and the association of metallization with the turnover of the Raman mode has been a red herring.

THE J=4 ROTON BAND

In the hydrogens the J=4 roton band normally cannot be observed, as the selection rule is $\Delta J=2$ and only J=0 and two rotational states are populated. By pressurizing a crystal of D₂ the melting temperature can be increased so that the J=2 band can be thermally populated before the crystal melts. We have done this to observe J=2→4 transitions³⁶ (Fig. 19). In the figure the dashed line shows the T=4.2 K background (the 00→22 feature is due to a double transition, unimportant for the present study). Since the J=4 band is very narrow (due to the weak coupling of molecules in this state to other molecules) the line width is due to the width of the J=2 band. A study of this width at very high pressures will be important for determining the mechanism of the BSP transition. It has been proposed that this is due to a soft roton at the Brillouin zone boundary. This should dramatically effect the linewidth at high pressure.

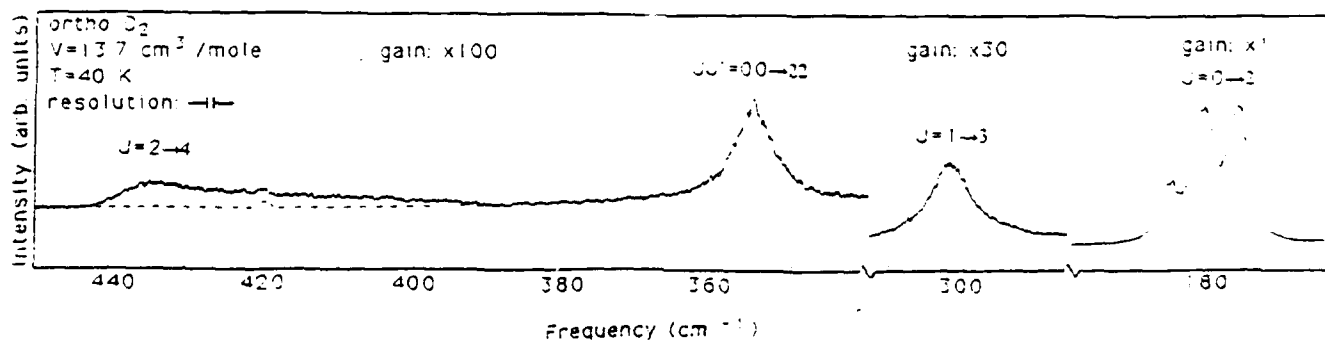


Figure 19

The Raman Spectrum of a Pressurized Ortho D₂ Crystal at T=40 K.

DEVELOPMENT OF NMR IN A DAC

In this final section we report on our development of NMR in a DAC. At this time the apparatus is essentially operational and the first NMR signals are being measured as a test of our design and construction. Our objective was to develop pulsed NMR for studying the very small samples of high pressure hydrogen. Due to the size of the sample a very sensitive apparatus, capable of signal averaging was designed. The design was split up into four parts discussed below: the magnet cryostat system; the DAC and suspension; the pulsed spectrometer; and the digital signal detection system.

Magnet Cryostat System

To optimize the NMR research on solid hydrogen a superconducting magnet system to achieve 4 tesla was designed. The magnet must have a large bore (4" id) to hold the DAC and the field must be uniform to better than 1 in 10^5 to enable measurements of expected spectra. The high field insures high sensitivity, as the resonance frequency scales with the field and the sensitivity is at least linearly increasing with frequency. The magnet was built by American Magnetics Inc. and has been tested, achieving almost 7 tesla, well beyond our specifications. It is equipped with a persistent mode switch. The magnet operates at 4.2 K in a vapor cooled cryostat supplied by Precision Cryogenics Inc (Fig. 20). Also shown is the anticryostat for warming the sample in a cold environment, the DAC and the DAC suspension.

DAC and Support System

The DAC used for this research must be non-magnetic to maintain the highly homogeneous field. We are using our BeCu cell. This has been modified to remove some magnetic components. In testing it was found that the diamonds do not maintain their alignment during the pressure stroke, required to achieve megabar pressures. The cell is currently being modified to improve its stability.

In the studies of hydrogen it is important to be able to change the temperature. The DAC will be cooled to 4.2 K in the bore of the sc magnet. To achieve higher temperatures we have built an anti-cryostat, a double-walled insert in which the DAC sits. If the walls are evacuated the DAC can be warmed to room temperature; if filled with helium thermal exchange gas the DAC will operate at 4.2 K. This was built in the Harvard Machine shop (Fig. 20).

The DAC is suspended from a special support (Fig. 20). This suspension enables the changing of the pressure while the DAC is at low temperature. It is fitted with a fibre optic system to allow excitation and detection of ruby for pressure measurement. It also enables in-situ tuning of the NMR circuit. Liquid helium can also be transferred in through the flange and pumped on to achieve temperatures as low as 1 K. This apparatus was constructed in the Harvard Machine shop.

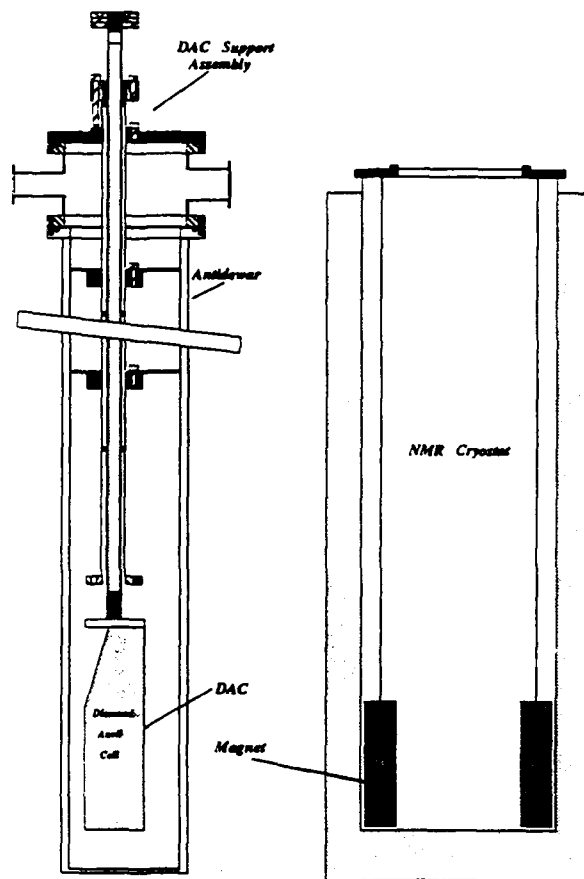


Figure 20

The Cryogenic System Including the SC Magnet and Cryostat on the Right.

NMR Spectrometer and Detection System

Figure 21 shows a block diagram of our electronic system for NMR which we have designed, assembled and tested. The main box holds a number of pc boards which we have designed and built to perform pulsed NMR. The system works as follows. An HP8640B frequency synthesizer delivers a cw sine wave signal at the resonance frequency (223 Mhz). The spectrometer board gates the signal on for a designated period of time to form the rf pulse. Actually a series of pulse trains can be created, depending on the type of measurement (spin-echoe and other sequences to enhance the signal detection and the nulling out of pick-up signals). The gating on and off is controlled by a series of pulses derived from a pulse generator which also sets the length and time between pulses. The particular type of measurement sequence can be dialed in on the pulse logic board. The phase-coherent pulse sequence is then directed to the ENI pulse power amplifier which delivers the signal

to the resonant circuit coil. After the energy from the pulse attenuates, the same coil detects the free induction of the spin system. This microvolt signal is first amplified by a low-noise preamp and then amplified up to a volt level. The signal is phase detected at 223 MHz so that the linewidth of the NMR line will determine the frequency band contributing to the output, typically 200 to 400 kHz. The linewidth puts reasonably stringent requirements on the digital sampling frequency, to acquire all of the information. The in-phase and out-phase signals are then fed into two fast (20 MHz) analog-digital converters. Since the signal is being acquired at a higher rate than can be transferred to the computer, the digital signals are fed into fast fifos (first in first out memories). In between each pulse train there is then ample time to read these values into the computer memory via a National Instruments interface board. The digital signals are then signal averaged and Fourier transformed to give the desired NMR line shapes.

As of the writing of this report the system is operational and test measurements are being made first on gypsum and then on solid hydrogen at zero pressure.

Block diagram of the NMR experiment.

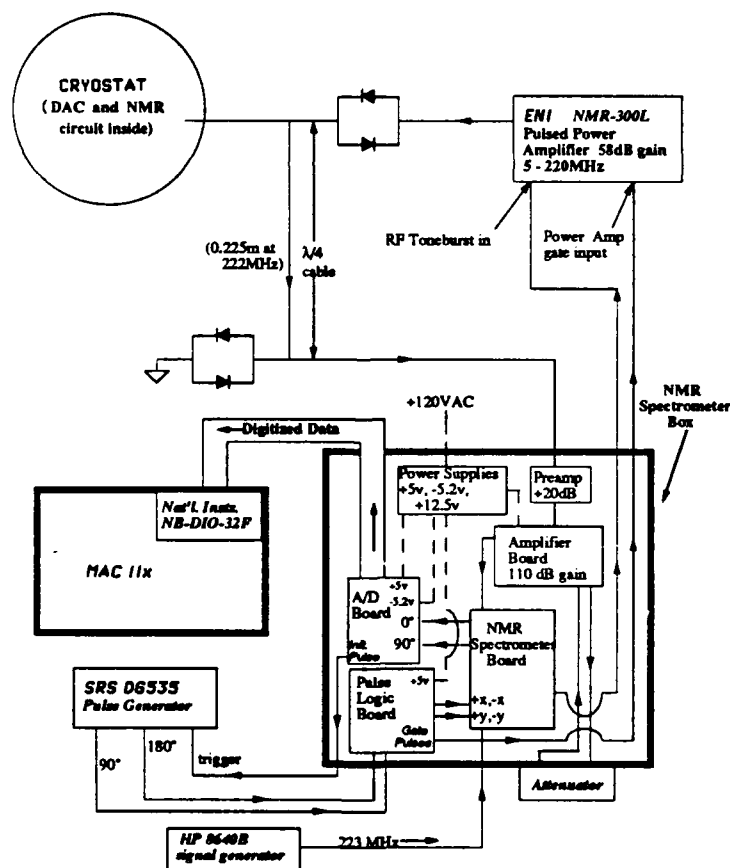


Figure 21

A Schematic Diagram of the Computer Controlled NMR system.

CONCLUSIONS

In the past three years, substantial advances have been made in the understanding of hydrogen at ultra high pressures. Hydrogen has been studied at pressures as high as 230 GPa. We have not yet reached a physical limitation to the pressure and expect that with care we shall be able to proceed to higher pressures in the 300-400 GPa range. This will eventually be necessary as one probes for the atomic metallic transition. This comment should be prefaced with the remark that we suspect that at room temperature hydrogen diffuses into diamond and embrittles it, limiting the pressures which can be achieved to 150-175 GPa. Thus, higher pressures will either require work at lower temperatures, ie of order 77 K or lower, or coating of the diamonds with a material which inhibits the diffusion of hydrogen into the diamond.

Three phases of hydrogen have been observed at megabar pressures. Due to the difficulty of making measurements under these extreme conditions, the phase lines have not all been carefully studied. The best studied is the H-A phase which may be the metallic molecular phase. This phase line has been found to have a critical point termination, which can be explained in terms of an IM transition. The BSP phase, long sought at lower pressures, since the observation of such a transition in deuterium at much lower pressures, has been found at 110 GPa at liquid helium temperatures. The disappearance of rotational intensity in this phase is not understood and requires further study. Finally an order-disorder transition of para-hydrogen has been observed within the H-A phase. The transition is not understood and is unexpected. A better understanding may arise from a study of how the three phase lines meet in P, T space. Another phase transition known from low pressure work, due to EQQ interactions in ortho hydrogen, has not yet been observed at high pressures.

Theoretical models of hydrogen are currently limited by lack of knowledge of the crystal structure. Dielectric measurements were made of the dispersion of the index as a function of pressure. These results have been compared to LDA electronic band structure calculations and show some agreement, but some differences. The results are very sensitive to the orientational order of the molecules and merit further study. In particular it is important to determine the index of refraction of hydrogen in the megabar range.

Advances in high pressure research are strongly related to the knowledge of the pressure. In DACs this is determined by the ruby spectrum of fluorescence. Although the ruby standard has been severely criticized in the past, we believe that our work in the past three years has shown that with careful work ruby can be used in the 200-300 GPa range and perhaps to even higher pressures. Currently this requires extrapolation of the calibration; calibrations to higher pressures would be very useful.

A high frequency pulsed NMR spectrometer has been constructed and is currently being tested for use in DACs. This should enable researchers to acquire new knowledge concerning high density hydrogen.

RECOMMENDATIONS

After more than 50 years of speculation and predictions of properties, advances in the pressurization and study of hydrogen in the past three years, using diamond anvil cell techniques, have proceeded rapidly. Due to the difficulty of studies under the extreme conditions of multimegabar static pressures and low temperatures, fascinating new properties found in recent years are not yet well understood. We recommend a continued experimental effort to clarify and advance the state of knowledge. Of particular interest is development of techniques to detect and characterize metal insulator transitions. The most rigorous experiments would measure the dc electrical conductivity in the limit that temperature goes to zero. Current optical techniques to study the Drude behavior from optical absorption and reflection experiments leave a great deal of uncertainty as at the present time the low frequency range of study has been too limited. Experiments should be developed with a more extended spectral range. The fascinating phase diagram of hydrogen which depends on ortho-para concentrations as well as pressure and temperature requires a better understanding. Only with a good understanding of this diagram can one hope to control the conditions for metallization and understand the metallization path. New experimental tools used in DAC research, such as NMR, if extendable to megabar pressures, should result in new insights and understanding of ortho-para conversion and order-disorder phase transitions. A final recommendation is for a continued effort to advance the pressure range accessible to experiment and the pressure determination techniques, a necessary step in studying the atomic metallic state.

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